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13 ABSTRACT (Maximum 200 words)

A novel, high yield synthetic scheme for poly(paraphenylene) starting from biologically produced cis-5,6-dihydroxy-1,3-cyclohexadiene has been developed in which trimethylsiloxy groups on the diol precursor polymer are quantitatively transformed to ester functionalities for facile cis-pyrolytic elimination. The final pyrolysis step appears to be very sensitive to reaction conditions and additives, and can result in some degradation of the polymer backbone. The use of Lewis acid salts such as anhydrous zinc halides or Bronsted acids such as 3,4-dichlorobenzenesulfonic acid as aromatization catalysts has been found to lower the aromatization temperature and prevent degradation. The Lewis acid salt catalysts afford dark colored, tough films while the Bronsted acid catalysts afford light colored, malleable foams. Polyphenylenevinylene has also been prepared from cis-5,6-dihydroxy-1,3-cyclohexadiene through a precursor polymer route.

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**Completed Project Summary (Final Technical Report)**

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## PUBLICATIONS:

(a). "Transition-Metal-Catalyzed Polymerization of Heteroatom-Functionalized Cyclohexadienes: Stereoregular Precursors to Poly(*para*-phenylene)." D.L. Gin, V.P. Conticello, and R.H. Grubbs, J. Am. Chem. Soc., 114, 3167-3169 (1992).

"Ring-Opening Metathesis Polymerization of Substituted Bicyclo[2.2.2]-octadienes: A New Precursor Route to Poly(1,4-Phenylene-Vinylene)." V.P. Conticello, D.L. Gin, and R.H. Grubbs, J. Am. Chem. Soc., 114, 9708-9710 (1992).

"Highly Unsaturated Oligomeric Hydrocarbons:  $\alpha$ -(Phenylethynyl)- $\omega$ -phenylpoly[1,2-phenylene(2,1-ethynediyl)]." R.H. Grubbs and D. Kratz, Chem. Ber., 126, 149-157 (1993).

"Polyparaphenylene by Metal Catalyzed Polymerizations." D.L. Gin, V.P. Conticello, and R.H. Grubbs, in preparation.

"Acid Catalyzed Conversion of Polycyclohexadienes to Polyparaphenylene" D.L. Gin, V.P. Conticello, and R.H. Grubbs, in preparation.

(b). Chapters

Transition Metal Catalyzed Polymerizations of Heteroatom-Submitted Cyclohexadienes: Precursors to Poly(paraphenylene)." D.L. Gin, V.P. Conticello, and R.H. Grubbs, *Polymer Preprints*, 32, 236-237( 1991).

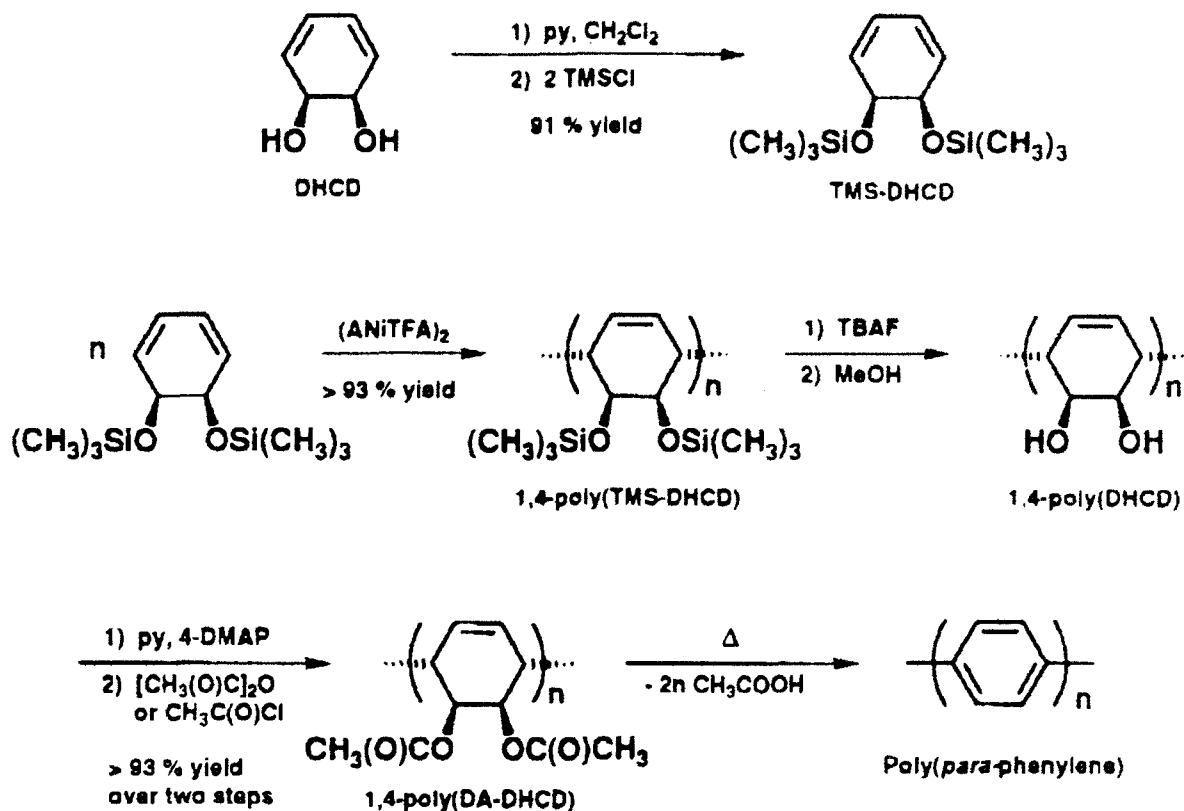
ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

**Polyparaphenylene**

For the past few years, our research group, in collaboration with ICI Chemicals and Polymers Ltd., has been investigating the possibility that transition-metal catalysts can be used to control the polymerization of *cis*-5,6-dihydroxy-1,3-cyclohexadiene (DHCD) derivatives to produce entirely 1,4-linked precursor polymers to poly(*para*-phenylene) (PPP). Our investigations thus far have met with great success, especially over the past year.

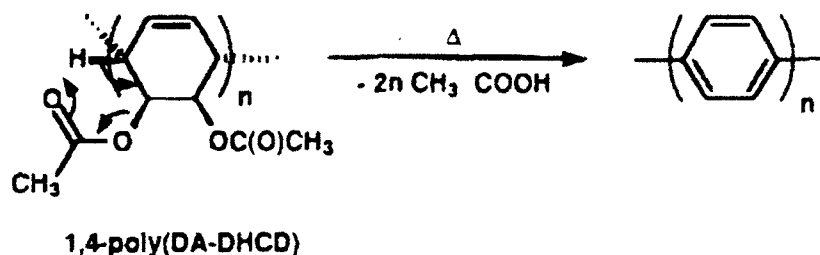
Our initial studies revealed that bis[(allyl)trifluoroacetatonickel II] (ANiTFA)<sub>2</sub>, a *p*-allyl catalyst which has shown some heteroatom compatibility in butadiene copolymerizations, is able to polymerize the bis(trimethylsilyl) derivative of DHCD, (TMS-DHCD), to yield a soluble polymer. <sup>1</sup>H NMR spectroscopy, powder X-ray diffraction, and STM imaging all correlated with molecular modeling, confirmed that the poly(TMS-DHCD) is entirely 1,4-linked as desired. However, since there is no simple elimination pathway for the loss of TMSOH, thermolysis experiments were unable to yield PPP directly from this new stereoregular polymer.

Over the past year, a novel high yield synthetic scheme for PPP has been developed in which the trimethylsiloxy groups on the 1,4-poly(TMS-DHCD) are quantitatively transformed to ester functionalities for facile *cis*-pyrolytic elimination to form PPP.



Scheme 1

Although preliminary experiments have demonstrated that our new methodology can indeed obtain the target polymer, additional work is required on this process before the PPP produced is suitable for technical applications. For example, the final pyrolysis step in the procedure, which was initially believed to be a straight forward process, now appears to very sensitive to reaction conditions and additives. We have found that this final step in the synthesis is as crucial in determining the purity of the final product as the precursor stereochemistry. Other important factors such as molecular weight control, morphology control, and processing also need to be addressed in order to obtain high quality PPP. Pyrolysis of thin films of the precursor on NaCl plates have yielded excellent PPP films as revealed by IR analysis. Although the stereochemistry of the 1,4-poly(DA-DHCD) lends itself to the seemingly straight forward *cis*-pyrolytic elimination, the aromatization reaction has in reality been found to be quite complex when large quantities of the polymer are involved.



Thermogravimetric analysis-mass spectrometry (TGA-MS) performed at ICI on bulk samples of 1,4-poly(DA-DHCD) revealed that the polymer backbone degrades upon pyrolysis. It exhibits greater than theoretical mass loss (if only acetic acid were produced) and generates phenol and phenyl acetate as the major elimination products well before acetic acid is detected. This chain scission is postulated to be the result of a radical process. In contrast, the major elimination product from the bulk pyrolysis of the radically polymerized acetoxypolymer is first acetic acid, followed by phenol and benzene side products. This result indicates that the stereoregular backbone of the 1,4-poly(DA-DHCD) is less thermally stable and more susceptible to homolytic cleavage than the random backbone of the radically polymerized analog. This is contrary to the original expectation. It appears as though the ceiling temperature (around 290°C) of the polycyclohexadienes is around that temperature required for acetate loss. This being the case, techniques for dropping the elimination temperature below the ceiling temperature are required.

Experiments involving the use of aromatization catalysts with the 1,4-poly(DA-DHCD) have yielded very promising results in overcoming this problem. When a small amount (2%) of a Lewis acidic salt such as an anhydrous zinc halide ( $\text{ZnX}_2$ ) is added to the 1,4-poly(DA-DHCD), the major elimination product is the expected acetic acid and only traces of phenol and phenyl acetate are present. The mass loss in this case levels off and approaches the theoretical value. The onset temperature ( $T_{\text{onset}}$ ) for the aromatization is also lowered considerably compared to the uncatalyzed case.  $T_{\text{onset}}$  values as low as 200 °C have been achieved by varying the percentage of  $\text{ZnX}_2$  added.

The PPP- $\text{ZnX}_2$  composite produced by the catalyzed aromatization is an extremely tough, amorphous, black material which is thermally stable up to the mid-400 °C range. The material can be obtained as smooth free standing films or hard foams due to a fluid tar-like metaphase observed during the conversion. IR analysis of the composites indicates that the PPP chains are of longer chain length than comparable PPP material obtained by pyrolyzing the radically polymerized acetoxypolymer. The

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aforementioned Zn catalyzed aromatization process is not limited to the stereoregular PPP precursors but it is also effective for the radically polymerized analogs.

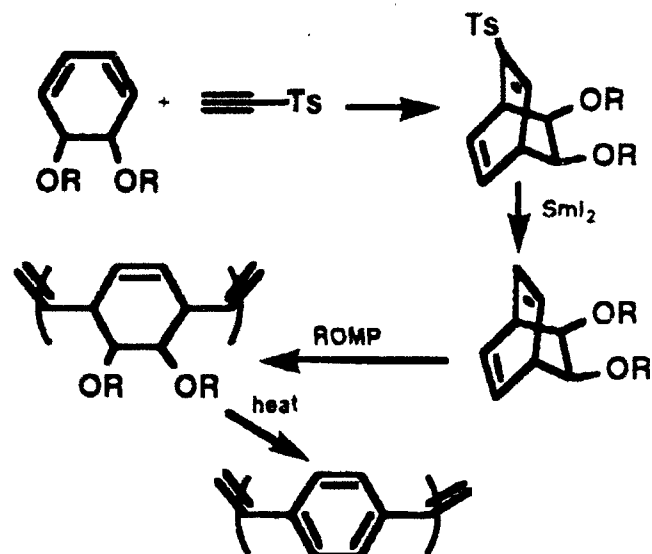
Similarly, experiments using Bronsted acids as aromatization catalysts for the conversion of 1,4-poly(DA-DHCD) to PPP have met with great initial success. The use of strong, nonvolatile protic acids as catalysts for the aromatization of the radically polymerized acetoxy-precursor was recently pioneered by Wilson *et al.* They observed that organic acid catalysts such as 3,4-dichlorobenzenesulfonic acid (DCBSA) effectively reduced the Tonset for the aromatization of the radically polymerized acetoxy-polymer and allowed for near theoretical mass losses. Their final products were highly colored, brittle free standing films.

The use of DCBSA with our stereoregular 1,4-poly(DA-DHCD) exhibited a similar effect as that observed by Wilson *et al.* However, the morphology of the PPP produced from the acid-catalyzed pyrolysis of the 1,4-poly(DA-DHCD) is markedly different. Instead of obtaining dark films, we were able to reproducibly obtain spongy foams, similar to an areo-gel, with lustrous golden fibers inside. These PPP "sponges" are soft and malleable and possess a remarkable thermal stability (only 3 % mass loss up to 500 °C under Ar). IR analysis of the "sponges" revealed that they are comprised of PPP of excellent chain length.

Through the use of aromatization catalysts, we not only have the means to produce high quality PPP under much milder conditions but also the potential to control the morphology of the final product. By simply varying the type of catalyst, we have been able to obtain tough films or malleable foams. To fully realize the potential of this process though, much work remains to be done. TGA-MS experiments have been performed. These TGA-MS experiments have helped elucidate the mechanism by which the catalysis occurs through identification of the elimination products. The final product has been fully characterized by solid state NMR spectroscopy and been shown to be high molecular weight material of the proposed structure.

### **Polyphenylenevinylene**

The 1CI cyclohexadiene monomer has been used to prepare polyphenylenevinylene through a precursor route. This route is being developed to yield a variety of substituted analogs that should be useful in photoemitting diodes.



Since the final conversion step can be catalyzed by acid or base, dependent on R, this route provides the opportunity to fabricate the material using photoresist technology.